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Photodegradation of *N*-Methyldiethanolamine over ZnO/SnO_2 Coupled Photocatalysts

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Abstract. *A photocatalyst semiconductor can be used to remove organic pollutants from wastewater in the presence of UV light. In this research, coupled ZnO/SnO_2 semiconductors with 1:1 and 2:1 ratios were prepared using the co-precipitation method. The prepared coupled ZnO/SnO_2 photocatalyst was tested towards the photodegradation of simulated N-Methyldiethanolamine (MDEA) under UV-irradiation ($\lambda = 365$ nm, 100 V, 6 W). The ZnO/SnO_2 was characterized using UV diffused reflectance spectroscopy and X-ray diffraction. The band gap energy for ZnO/SnO_2 (ZS) catalyst calcined at 200° C, 400° C, 600° C and 900° C were 3.22, 3.13, 3.12 and 3.07 eV, respectively, while for Z_2S were 3.71, 3.28, 3.16, and 3.14 eV, respectively. XRD results indicated that ZS and Z_2S catalysts possessed mixed phases of ZnO, SnO_2 and Zn_2SnO_4 at a calcinations temperature above 600° C. The ZnO/SnO_2 (2:1) catalyst, which was calcined at 600° C for 9 hours, gave the optimum percentage photodegradation of MDEA with 39.18%. The percentage degradation of MDEA was measured using ion chromatography with retention time at the measured peak of 4-5 minutes. The optimum system was applied on the photodegradation of MDEA in petroleum wastewater. The percentage degradation of MDEA in petroleum wastewater was 23.38 %.*

Keywords: *ZnO; SnO_2; MDEA; Photocatalyst; Photodegradation; Band gap energy.*

INTRODUCTION

N-MDEA is one organic pollutant commonly used in petroleum processing industries as a chemical for the removal of CO_2 and H_2S. It may be found in processed water that is then transported to the wastewater treatment plant, which can cause a major reduction in the effectiveness of ammonia stripping and biological filter performance. In the past decade, there have been a number of studies related to the photocatalytic activity of TiO_2 or ZnO coupled with metal oxides like SnO_2, WO_3, Fe_2O_3, ZrO_2 and some rare earth oxides [1]. The photocatalytic enhancement is due to an increase in charge separation and the extent of the photo-responding range.

Tennakone and Bandara [2] reported that the ZnO/SnO_2 composite was active in the sensitization degradation of dye molecules. ZnO/SnO_2 catalytic activity was superior to individual ZnO, SnO_2 or TiO_2 particles, and its higher catalytic activity was assigned to the wider charge separation ability of the composite ZnO/SnO_2 system. Wang et al. [1] had studied the photocatalytic activity of ZnO/SnO_2 coupled oxide with different Sn content prepared by the co-precipitation method of preparation to degrade Methyl Orange (MO) as the model organic compound. As a result, coupled ZnO/SnO_2 with 33.3 mol% Sn content calcined at 500°C for 10 hours was found to be relatively stable and an effective photocatalyst for the degradation of MO. Cun et al. [3] also studied the photocatalytic activity of ZnO/SnO_2 with the same co-precipitation method of preparation on the degradation of MO, but using a different ratio of Zn. It was found that the photocatalytic degradation rate of MO on Z_2S was faster than the ZS ratio. So far, no report for the degradation of MDEA has been reported.

This paper aims to study further the performance of a coupled ZnO/SnO_2 photocatalyst on the degradation of the N-MDEA presence in petroleum wastewater. Furthermore, the effect of different band gap energy on the photocatalytic activity of the prepared catalysts was studied and related to the degradation results.

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EXPERIMENTAL

Chemicals

The chemicals required to prepare the ZnO/SnO_2 coupled catalysts (ratio 1:1 and 2:1) were $ZnSO_4.7H_2O$, $SnCl_4.5H_2O$ and sodium hydroxide (NaOH). N-methyldiethanolamine (MDEA) was purchased from Merck with 98 wt% purity. Petroleum wastewater was collected from the Petronas Refinery, Melaka Pte. Ltd., Malaysia.

Preparation of ZnO/SnO_2 Coupled Catalysts (Ratio 1:1 and 2:1)

The coupled oxide photocatalyst ZnO/SnO_2 (ratio 1:1) was prepared by the co-precipitation method. $SnCl_4.5H_2O$ and $ZnSO_4.7H_2O$ were used as starting materials with NaOH as the co-precipitant. The addition process was conducted in an ice bath because of the hygroscopic properties of the precursors and to obtain a better catalyst. All chemicals were used without further purification. $ZnSO_4.7H_2O$ and $SnCl_4.5H_2O$ in molar ratios of 1:1 or 1:2 were dissolved in a minimum amount of deionized water. Then, the NaOH solution was added dropwise with a flow rate of 2 mL/min into the above solution to adjust the pH in order to obtain a pH of the solution of about 7. At pH 7, a white precipitate was formed. The pH solution was measured using a pH meter; Mettler Toledo model FE20.

The precipitate was filtered and washed with deionized water until no SO_4^{2-} and Cl^- ions were found in the filtrate. The wet solid was aged at ambient temperature for 24 hours and, then, in the oven at 100°C for 12 hours to form the precursor of the ZnO/SnO_2 (ratio 1:1) coupled photocatalyst. Finally, the precursor was grounded to form powder and calcined in the furnace at various temperatures (200°C, 400°C, 600°C and 900°C for 9 hours) to produce the ZS and Z_2S (ratio 1:1 and 2:1) coupled photocatalysts.

Photocatalytic Activity of MDEA

For the degradation of MDEA, a solution of MDEA (1000 ppm) and the semiconductor photocatalyst (1.5 g/L) was transferred into a 250 mL beaker. The solution was allowed to equilibrate in the dark for 30 minutes. Then, 5 mL of the solution were taken and filtered with a millipore membrane (0.45 μm) before transferring the filtrate into a bottle sample. After that, irradiation was carried out using a 12W UV-lamp, with a wavelength of 365 nm, which was placed above the beaker containing the solution. During the irradiation process, agitation was maintained using a magnetic bar to keep the suspension homogenous. A sample of the suspension was taken after an appropriate illumination time and filtered through a membrane filter to remove the catalyst. The filtrate was then analyzed.

The degradation of MDEA using photolysis, adsorption and a photocatalyst in each degraded sample was determined using ion chromatography (METROSEP Cation Dual 2) with the measured peak at a retention time of 4-5 minutes. Verification of the degradation was carried out using a Total Organic Carbon (TOC) Analyzer; model TOC-V_E, Shimadzu. The percentage of degradation of MDEA was obtained at different time intervals. The percentage of degradation of MDEA as a function of time is given by:

$$\%\text{degradation of MDEA} = \frac{C_o - C_t}{C_o}, \quad (1)$$

where:

C_o = initial concentration of sample,
C_t = concentration of sample at time t.

Characterization of ZS and Z_2S

To determine the band gap energy of the prepared photocatalysts, a UV-VIS diffused reflectance spectrometer measurement was carried out using a Perkin Elmer, Lambda 900. The pure $BaSO_4$ was used as the blank sample. The wavelengths of the absorption edges were determined by extrapolating the horizontal and sharply raised portions of the curve and defining the edge as the wavelength of the intersection [4]. The scale labeled "absorbance" means the negative logarithm value of the experimentally determined diffuse reflectance of samples [5].

A Siemens D5000 X-Ray Diffraction (XRD) was used to identify the crystalline phase and structural properties of the prepared catalyst. Each catalyst sample (fine powder) was distributed on the surface of the sample holder by using a piece of glass, and was placed onto a Siemens D5000 X-ray diffractometer equipped with Cu-K_α (1 = 1.54 Å) radiation. Data were collected over the 2θ range of 15° to 80° using a 40 KV and 30 mA source.

RESULTS AND DISCUSSION

Photocatalytic Activity of the Photocatalyst

Figure 1 shows the percentage of degradation of MDEA using direct photolysis, adsorption of the MDEA catalyst and photocatalytic degradation using UV and ZnO, SnO_2, ZS and Z_2S catalysts. From observations, no degradation of MDEA was observed in the absence of the catalyst (photolysis) or in the absence of UV light (adsorption).

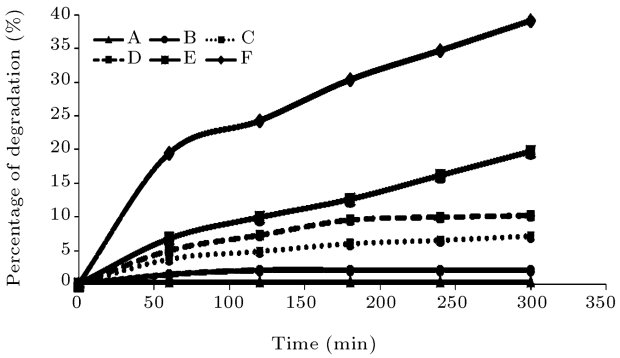

Figure 1. The percentage degradation of MDEA. A: Photolysis; B: adsorption of Z_2S 600°C, 9h; C: UV+ SnO_2; D: UV+ ZnO; E: UV+ ZS, 600°C, 9 hours; F: UV + Z_2S, 600°C, 9 hours.

It can be seen that the Z_2S catalyst was a more effective photocatalyst for the degradation of MDEA, which gave 39.18% degradation, compared to ZnO, ZS, and SnO_2, which only gave 19.72%, 10.22% and 7.07%, respectively. The Z_2S catalyst that was calcined at 600°C for 9 hours (Figure 1) showed a drastic increase in the rate of degradation for 1 hour of irradiation time; up to 20% of the MDEA photodegradation. After 2 hours of irradiation, the percentage of degradation was slightly increased to 24%. The percentage degradation increased constantly for another 1 hour of irradiation time. After 5 hours of UV irradiation, the percentage of MDEA degradation, using the Z_2S catalyst calcined at 600°C for 9 hours, was 39.18%. SnO_2 shows low photocatalytic activity, which agrees with the literature result [3]. Wu [6] also documented that the small amount of degradation, using SnO_2 as the photocatalyst, was attributed to the band gap energy (4.13 eV) of SnO_2, which was insufficient for initiating the photocatalytic reaction after using 365 nm UV- irradiation. In addition, SnO_2 had lower photocatalytic activity due to the fast recombination of the photogenerated electron/hole pairs. According to Figure 1, the Z_2S semiconductor photocatalyst was a better photocatalyt than the single ratio of the ZS photocatalyst. The small percentage degradation of MDEA was attributed to the same phase composition of the ZS photocatalyst, which were only Zn_2SnO_4 and SnO_2 species, as mentioned in the characterization. The reason for the significant reduction of the photocatalytic activity of the ZS photocatalyst was found to be similar to previous research findings due to the formation of the Zn_2SnO_4 species [1]. The Zn_2SnO_4 species possessed a larger particle size and lower surface area. Other than that, when the calcination temperature was higher than 700°C, both the ZnO and SnO_2 oxides were partly transformed to Zn_2SnO_4, which is a poor photocatalyst [5]. In this study, a single ZnO photocatalyst gave better degradation than the single ratio of a coupled ZnO/SnO_2 photocatalyst. These findings agree with previous research, which found that the rate constant, k, of ZnO is similar to the coupled oxide ZnO/SnO_2, although the photocatalytic activity of ZnO was better than ZnO/SnO_2 in the degradation of Procion Red MX-5B at pH 10 [6]. Moreover, coupled ZnO/SnO_2 with Z_2S ratios was still a better catalyst for the degradation of MDEA. This was because when two oxides of ZnO and SnO_2 are coupled, the charge separation is more efficient. Thus, the recombination of electrons and holes of ZnO/SnO_2 was greatly suppressed [5]. This process occurred when the Conduction Band (CB) position of SnO_2 was lower than that of ZnO, so the former could act as a sink for the photogenerated electrons in the coupled oxides [2,7,8]. Since the holes move in the opposite direction from the electrons, the photogenerated holes in SnO_2 may be trapped within the ZnO particle.

Effect of Calcination Temperature on the Photodegradation of MDEA

The effect of calcination temperature on the photocatalytic activity of Z_2S is shown in Figure 2. The experiments were conducted at 200, 400, 600 and 900°C calcination temperatures.

It can be seen that the degradation of MDEA increased by increasing the calcination temperature to 600°C, and the photocatalytic activity of Z_2S decreased at the calcination temperature of 900°C. The significant decrease in the photocatalytic activity of Z_2S calcined at 900°C was only 10.02%, and this was attributed to variation in the phase composition and particle size with increasing calcination temperature [7]. The main reason for the decrease in the percentage of MDEA degradation, using catalyst calcined temperatures up to 900°C, was that all the ZnO reacted with SnO_2 forming binary Zn_2SnO_4 with low photocatalytic activity [3,9]. At 600°C, the percentage degradation of MDEA was the highest, i.e. 39.18%. This is because

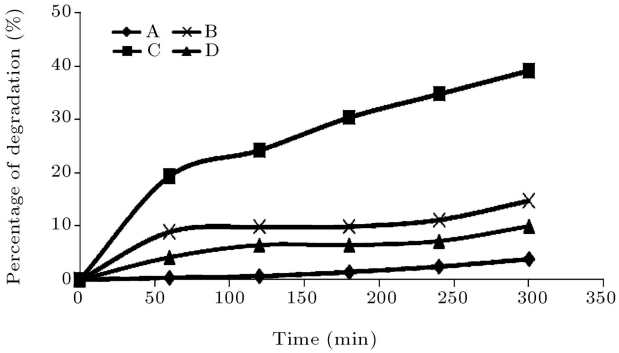

Figure 2. The effect of calcination temperature on the photodegradation of MDEA; A: Z_2S, 200°C, 9 hour; B: Z_2S, 400°C, 9 hour; C: Z_2S, 600°C, 9 hours; D: Z_2S, 900°C, 9 hour.

the photocatalyst consists mainly of ZnO and SnO_2, and less Zn_2SnO_4 phase was detected. Furthermore, by taking into account the XRD results, the increase in photocatalytic activity observed for the Z_2S catalyst at 600°C for 9 hours might be attributed to the formation of a well crystallized ZnO/SnO_2 system, a combination of two oxides and intermetallic phases that consist of ZnO, SnO_2 and less Zn_2SnO_4. However, at 900°C, the percentage of degradation of N-MDEA decreased because Zn_2SnO_4 was found to dominate at temperatures above 700°C, and photocatalytic activity was inhibited by the catalyst [10]. At 200°C, the photocatalytic activity of Z_2S was the lowest, compared to other photocatalysts calcined at 400°C and 600°C. This was because at this temperature the catalyst was still in the amorphous phase.

Photocatalytic Treatment of Real Petroleum Wastewater

The photocatalyst, Z_2S, calcined at 600°C for 9 hours was applied to the photodegradation of petroleum wastewater containing a high concentration of *N*-methyldiethanolamine. The petroleum wastewater sample was obtained from the Petronas refinery, Malacca, Malaysia. The pH of the petroleum wastewater was similar to the pH of the simulated MDEA which was 9.28. The green solution of the petroleum wastewater was in an alkaline condition. Figure 3 shows the percentage degradation of N-MDEA in the petroleum wastewater.

The percentage degradation of N-MDEA was only 23.38% in petroleum wastewater after 5 hours of irradiation. Compared to the simulated system, the percentage degradation of MDEA in petroleum wastewater was found to be lower than simulated MDEA (39.18%) at the same concentration, i.e. 1000 ppm. This was because the real petroleum wastewater contained highly concentrated N-MDEA and several hydrocarbons. The other reason is because the lower percentage of N-MDEA degradation in the petroleum wastewater might be due to the adsorption, degradation or oxidation and reduction of other hydrocarbons present in the petroleum wastewater, which cause competition between N-MDEA and the hydrocarbon for the photocatalyst, Z_2S.

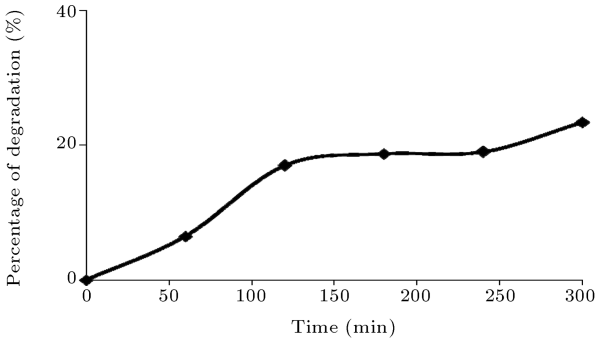

Figure 3. Percentage degradation of MDEA in petroleum wastewater using catalyst Z_2S, 600°C, 9 hours under 300 minutes irradiation time.

Total Organic Carbon Elimination

Figure 4 shows the TOC elimination of MDEA photocatalytic degraded by Z_2S calcined at 600°C for 9 hours, in petroleum wastewater and simulated systems. The percentage mineralization of N-MDEA in real wastewater and simulated N-MDEA was 23.15% and 22%, respectively, after 5 hours irradiation time.

Moreover, the mineralization of N-MDEA was very slow in the petroleum wastewater system after 180 minutes irradiation time. Noticeably, 76.85% of TOC still remained. This observation might indicate the formation of some long-lived by-products, which have a low rate constant for the reaction with the hydroxyl radical [1]. For the simulated system, mineralization did not occur further after 120 minutes. irradiation time to form other inorganic species or carbon dioxide, which indicated that 78% of TOC still remained. From the experimental results, it became evident that some MDEA was mineralized into other intermediate or end products that were more harmless [11], such as CO_2, and all nitrogen containing compounds might form ammonium and nitrate ions upon photocatalytic degradation [12]. The percentage mineralization of N-MDEA was relatively low, because it was a highly stable compound, and the formation of other small organic compounds, when irradiated under UV light, might cause little change in TOC results.

Characterization of ZnO/SnO_2 Photocatalysts

The UV-vis diffused reflectance spectra of ZS and Z_2S calcined at 200, 400, 600 and 900°C are displayed in Figure 5. The absorption edge and band gap energies

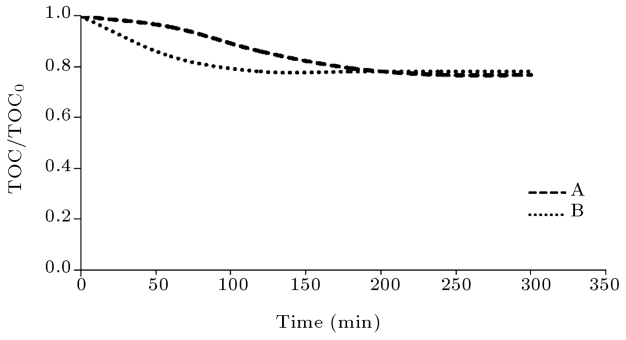

Figure 4. The TOC for the photocatalytic degradation of MDEA by A: Z_2S, 600°C, 9 hours in petroleum wastewater, and B: Z_2S, 600°C, 9 hours in simulated system.

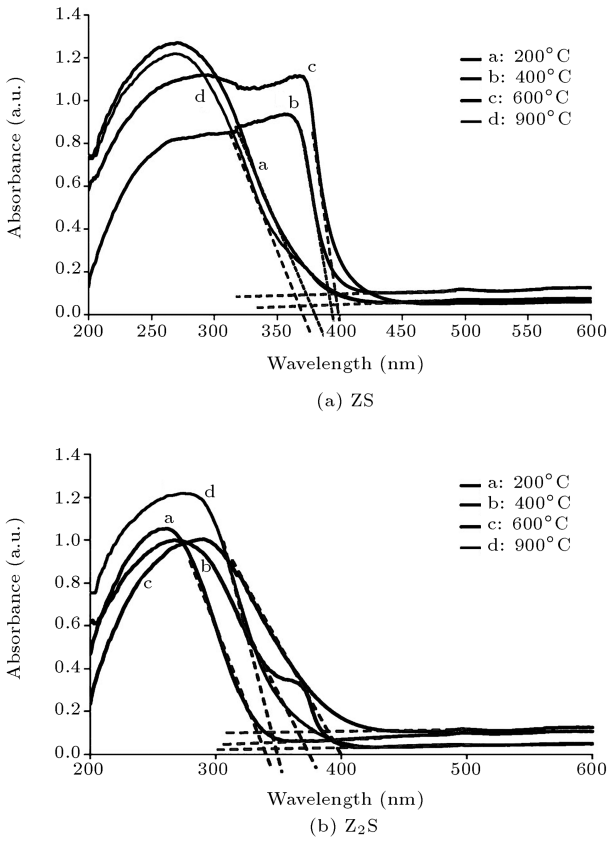

Figure 5. UV-vis diffuse reflectance absorption spectra of the coupled ZnO/SnO_2 photocatalyst powder calcined at different temperatures for 9 hours.

of ZS and Z_2S, calcined at different temperatures and times, are listed in Table 1. The catalyst calcined at 400, 600 and 900°C for 9 hours contained a mixture of ZnO, SnO_2 and/or Zn_2SnO_4. Thus the band gap energies of the coupled ZnO/SnO_2 photocatalyst should originate from an overlapping of the corresponding ZnO, SnO_2 and or Zn_2SnO_4 components in coupled oxides [1]. From the experimental data, it is found that the difference in the band gap energy might be due to a change in the ratio of ZnO, SnO_2 or Zn_2SnO_4 in the coupled oxide photocatalyst, which was controlled by the Zn content and calcination temperature. The band gap energies for ZnO, SnO_2 and Zn_2SnO_4 were reported to be 3.2eV [3], 2.53 eV [1] and 3.4 eV [1], respectively. As shown in Table 1, it is found that for both ZnO/SnO_2 catalysts with ZS and Z_2S ratios, the absorption edge increased with increasing calcination temperatures. Furthermore, reduction in the band gap of a semiconductor affected most semiconductor material parameters. The decrease in the band gap of a semiconductor with increasing temperature could be viewed as increasing the energy of the electrons in the material. From the result, the absorption edges of ZS and Z_2S calcined at 600°C for 9 hours were determined to be 398 nm and 393 nm, corresponding to the band gap energies of 3.12 and 3.16 eV, respectively. According to the literature [4,13], the adsorption edge for Z_2S was determined to be 394 nm, corresponding to the band gap energy of 3.15 eV [3]. From Table 1, it can be seen that the band gap energy for Z_2S is not the same as for ZnO or SnO_2. Similarly, the band gap energy for ZS was also neither of Zn_2SnO_4 nor of SnO_2. According to the previous study, ZS calcined under 600°C for 10 hours was comprised of Zn_2SnO_4 and SnO_2 and for Z_2S, consisted of ZnO and SnO_2 [3]. The band gap energies of materials were related to the photocatalytic activity of materials for degradation of the pollutants. The optimum band gap energy for this research was for the Z_2S catalyst (3.16 eV), which was calcined at 600°C for 9 hour, according to the higher percentage degradation of N-MDEA.

Table 1. Absorption edges and band gap energies of coupled oxides calcined at different temperatures.

Sample	Temperature (°C)	Absorption Edge (nm)	Band Gap Energy (eV)
ZS	200	385	3.22
	400	396	3.13
	600	698	3.12
	900	404	3.07
Z_2S	200	334	3.71
	400	378	3.28
	600	393	3.16
	900	395	3.14

Band gap energy for ZnO= 3.2 eV [3],
SnO_2= 2.53 eV [3],
Zn_2SnO_4=3.4 eV [3].

In order to understand the crystalline structure of the oxide catalysts, a XRD characterization technique was used. Information regarding the crystalline phases under various conditions was obtained by comparing the *d* value of the materials with those phases from the Powder Diffraction File (PDF). The X-ray diffraction patterns for ZS and Z_2S catalysts calcined at various temperatures are shown in Figures 6 and 7.

The ZS and Z_2S catalyst was analyzed using XRD in order to determine active oxide phases, which contributed to the enhancement of catalytic activity. From Figures 6 and 7, it was observed that the degree of crystallinity of all studied catalysts improved as they were calcined at higher temperatures (200°C, 400°C, 600°C and 900°C). A high crystalline phase was only observed for the catalyst calcined at 900°C, whereas the catalyst calcined at 200°C and 400°C showed an amorphous phase, and those calcined at 600°C showed a weak crystalline phase.

For ZS and Z_2S catalysts calcined at 200°C and 400°C, the phase was highly amorphous and no significant peak could be assigned. From Figure 6,

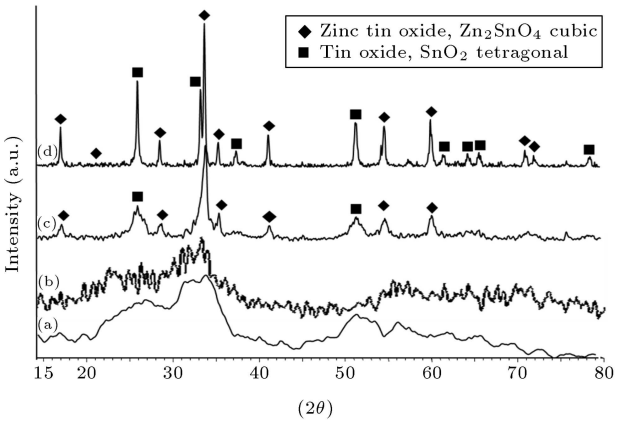

Figure 6. The XRD diffractogram for catalyst ZS calcined. (a) 200°C; (b) 400°C; (c) 600°C; (d) 900°C.

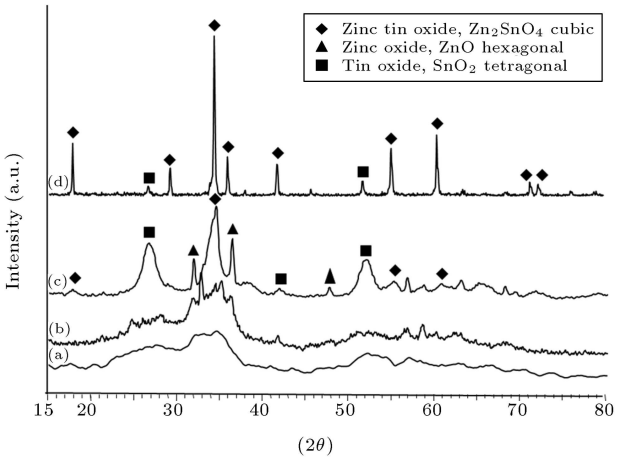

Figure 7. The XRD diffractogram for catalyst Z_2S calcined. (a) 200°C; (b) 400°C; (c) 600°C; (d) 900°C.

at 600°C, a mixture of the Zn_2SnO_4 cubic phase was observed at the 2θ value of 34.402°(I_{100}), with a d_{obs} value of 2.60 $\mathring{A}$(d_{ref} value 2.61 $\mathring{A}$), and SnO_2 at the 2θ value of 26.58°($I_{37.9}$), with a d_{obs} value of 3.35 $\mathring{A}$(d_{ref} value of 3.35 $\mathring{A}$). For the catalyst calcined at 900°C, a Zn_2SnO_4 cubic phase was detected at 2θ values of 34.361°(I_{100}), with d_{obs} value of 2.61 $\mathring{A}$(d_{ref} value of 2.61 $\mathring{A}$), and SnO_2 at 2θ values of 26.65 (I_{59}) and 33.94°($I_{54.5}$), with d_{obs} values of 3.34 and 2.64 $\mathring{A}$(d_{ref} values of 3.36 and 2.64 $\mathring{A}$). At a higher calcination temperature of 900°C, more peaks due to the Zn_2SnO_4 cubic phase were observed at 2θ values of 34.38 (I_{100}), 60.47 ($I_{38.1}$) and 17.73°($I_{32.9}$), with d_{obs} values of 2.61, 1.53 and 4.99 $\mathring{A}$(d_{ref} values of 2.61, 1.53 and 4.99 $\mathring{A}$). There was a mixture of phases of Zn_2SnO_4, ZnO and SnO_2 for the catalyst calcined at 600°C. The Zn_2SnO_4 cubic phase was observed at 2θ values of 34.42°(I_{100}), with the d_{obs} value of 2.60. The SnO_2 tetragonal phases were at 2θ values of 34.09 (I_{97}) and 26.713°(I_{67}), with d_{obs} values of 2.63 and 3.33 $\mathring{A}$(d_{ref} values of 2.64 and 3.34 $\mathring{A}$), while the ZnO hexagonal phase observed was at 2θ values of 36.355 ($I_{70.2}$) and 31.88°($I_{53.5}$), with d_{obs} values of 2.47 and 2.80 $\mathring{A}$(d_{ref} values of 2.48 and 2.81). From this study, for the Z_2S catalyst, the mixture of Zn_2SnO_4, ZnO and SnO_2 in one phase gave better degradation results (Figure 1), even though the intensity of Zn_2SnO_4 was higher than that of ZnO and SnO_2. This indicated that the Z_2S catalyst calcined at 600°C for 9 hours was a potential catalyst for the degradation of MDEA.

CONCLUSION

The photocatalyst ZnO/SnO_2, with ratio 2:1 and calcined at 600°C for 9 hours, was a promising catalyst for MDEA treatment, which gave 39.18% degradation. The photocatalyst possessed a band gap of 3.16 eV. The optimum calcination temperature for the photocatalyst was 600°C for 9 hours. A higher calcination temperature (900°C) gave the lowest photocatalytic activity, where only 10.2% MDEA was degraded. The mineralization of MDEA in simulated and petroleum wastewater was lower than its percentage of degradation.

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S.S. Mislan. His/her biography was not available at the time of publication.

M.A. Sharifuddin. His/her biography was not available at the time of publication.